

Ethylene Polymerization in the Presence of Iron(II) 2,6-Bis(imine)pyridine Complex: Structures of Key Intermediates¹

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Abstract—The structures of intermediates generated by the activation of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron(II) chloride (**1**) with various cocatalysts, methylalumoxane (MAO), trimethylaluminum (TMA), and TMA in combination with $B(C_6F_5)_3$ and $Ph_3CB(C_6F_5)_4$, is studied by 1H and 2H NMR spectroscopy. The $1/AlMe_3$ system exhibits a higher catalytic activity in ethylene polymerization than the $1/MAO$ system. The activity of the latter decreases sharply with a decrease in the amount of $AlMe_3$ in MAO. Neutral Fe(II) complexes rather than cationic intermediates are suggested to be active components in both catalytic systems.

INTRODUCTION

Iron(II) complexes with tridentate bis(imine)pyridine ligands activated by methylalumoxane (MAO) are stable and very active catalysts of ethylene oligomerization and polymerization [1–4]. However, experimental data on the nature of the active component of these catalytic systems are lacking. In this work, we present the first 1H and 2H NMR characterization of the iron complexes generated by the activation of 2,6-bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron(II) chloride (**1**) by various cocatalysts: MAO, trimethylaluminum, $AlMe_3/B(C_6F_5)_3$, and $AlMe_3/CPh_3B(C_6F_5)_4$. In addition, data on ethylene polymerization in the presence of these catalytic systems are presented.

EXPERIMENTAL

Reagents and Solvents

Methylene dichloride, methylene dichloride- d_2 , and toluene- d_8 were dried with P_2O_5 and distilled. Tetrahydrofuran (Aldrich) was kept above KOH, distilled, and shaken with $LiAlH_4$. Pentane (analytical grade) was treated with P_2O_5 , filtered, kept above sodium, and distilled. Diethyl ether was treated with KOH and P_2O_5 and distilled. 2,6-Diacetylpyridine, 2,6-dimethylaniline, and $FeCl_2(H_2O)_4$ were used as received (Aldrich). Methylalumoxane was commercially available from Witko (Berghamen). Operations with solvents along with their storage was carried out in a vacuum. All experiments were carried out in hermetically sealed evacuated glassware.

Synthesis

of 2,6-Bis[1-(2,6-Dimethylphenylimino)ethyl]pyridine

2,6-Diacetylpyridine (1.0 g, 6.1 mmol) and 2,6-dimethylaniline (3 ml, 24.4 mmol) were placed in a constant-temperature flask with a magnetic stirrer filled with methanol (30 ml). Then, 99% formic acid (5 drops) was added, and the solution was stirred at 50°C overnight. Afterwards, the solution was cooled in a vessel with ice. A lightyellow precipitate was filtered off, washed with cold methanol and pentane, and dried in a vacuum. The yield was 1.70 g (75%).

Synthesis of 2,6-Bis[1-(2,6-Dimethylphenylimino)ethyl]pyridineiron(II) Chloride

The obtained tridentate ligand (0.39 g, 1.05 mmol) was dissolved in tetrahydrofuran (25 ml) in an argon atmosphere, and $FeCl_2(H_2O)_4$ (0.2 g, 1.0 mmol) was added. The color of the solution turned immediately from yellow to dark blue. The mixture was stirred at room temperature in an argon atmosphere in a closed flask for several hours. The precipitate formed was filtered off in air, washed with diethyl ether and pentane, and dried in a vacuum. 2,6-Bis[1-(2,6-dimethylphenylimino)ethyl]pyridineiron(II) chloride (**1**) was obtained as a violet-green powder in 100% yield (0.5 g).

Preparation of MAO and $AlMe_3$ Samples

The MAO-1 sample was commercially available from Witko as a solution in toluene with a total aluminum concentration of 1.8 mol/l (~0.5 mol/l aluminum was in the form of $AlMe_3$).

The MAO-2 sample was prepared by drying the MAO-1 sample in a vacuum at 20°C. The solid product obtained was dissolved in purified deuterated solvents

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(the total concentration of Al in the solution was 0.1 mol/l, including that in the form of AlMe_3 of 0.01 mol/l).

The MAO-3 sample was prepared by drying the MAO-1 in a vacuum of sample at 50°C. A solution of MAO-3 in toluene (the total concentration of Al was 0.1 mol/l, including that in the form of AlMe_3 of 0.003 mol/l) was used for ethylene polymerization.

According to the ^1H NMR data, the liquid fraction obtained by drying the MAO-1 sample in a vacuum is a solution of AlMe_3 in toluene (Al concentration 0.4 mol/l). This fraction was used as an AlMe_3 sample.

$\text{Al}(\text{CD}_3)_3$ (99% D) was prepared by the interaction of CD_3I (99% D) with aluminum powder at 80°C and then with metallic sodium at 100°C followed by the vacuum distillation of the target product.

*Preparation of 1/MAO, 1/AlMe₃, 1/Al(CD₃)₃,
1/AlMe₃/B(C₆F₅)₃, and 1/AlMe₃/CPh₃B(C₆F₅)₄
Samples and NMR Measurements*

The desired amounts of complex **1** and a solution of MAO-2, AlMe_3 , $\text{Al}(\text{CD}_3)_3$, $\text{AlMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$, or $\text{AlMe}_3/\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$ in toluene- d_8 or CD_2Cl_2 were mixed directly in an NMR tube in a vacuum at a low temperature (−80 to −30°C). Then, the tube was sealed from the vacuum system and placed in a spectrometer. The concentration of Fe in the **1**/ AlMe_3 and **1**/MAO-2 catalytic systems was 0.0003–0.003 mol/l, and that of aluminum was 0.5–3.0 mol/l. The concentrations of $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$ in the **1**/ $\text{AlMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ and **1**/ $\text{AlMe}_3/\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$ catalytic systems were approximately equal to the concentration of **1** (0.001 mol/l), and that of AlMe_3 was 0.1 mol/l.

^1H and ^2H NMR spectra were recorded at 400.13 and 61.4 MHz using a Bruker MSL-400 spectrometer in the spectral range of 125 kHz. The accumulation frequency was 20 Hz (^1H) or 2.5 Hz (^2H), the storage number was 5000–20000, and 20°–40°-pulses with a duration of 5 μs (^1H) or 10 μs (^2H) were used. The chemical shifts of ^1H were timed from the signals of residual CHDCl_2 (5.27 ppm) or $\text{CHD}_2\text{C}_6\text{D}_5$ (2.1 ppm (CH_3)) in deuterated solvents. The chemical shifts of ^2H were read off from the deuterium signal of the solvent (the natural concentration of ^2H). The error in the determination of chemical shifts was ± 0.1 ppm for lines with a width of at most 200 Hz.

Ethylene Polymerization

Ethylene was polymerized in a 1-liter autoclave. Complex **1** (0.001 g, 2.0×10^{-6} mol) in an evacuated sealed glass tube was placed into the autoclave. The autoclave was evacuated at 50°C and cooled to 20°C. Then, a solution containing the calculated amount of the cocatalyst in toluene (150 ml) was poured into the autoclave. When temperature reached 35°C, ethylene was admitted to the reactor to a pressure of 5 atm. The

reaction started after the tube containing complex **1** was broken. The ethylene pressure and temperature were kept constant during polymerization. The polymerization conditions are presented in more detail in Table 2.

RESULTS AND DISCUSSION

^1H NMR Spectrum of Initial Complex 1

The ^1H NMR spectrum of the initial complex **1** (0.003 mol/l, CD_2Cl_2) (Fig. 1a) contains six narrow paramagnetically shifted signals ($\Delta\nu_{1/2} = 20\text{--}50$ Hz), which can unambiguously be assigned to the corresponding protons of the tridentate ligand on the basis of the data on the integral intensity and relative distance to the disturbing paramagnetic center (Table 1, spectrum 1).

Interaction of 1 with MAO

New complex **2** (Fig. 1b) is formed immediately in the reaction of **1** with MAO-2 in CD_2Cl_2 at room temperature ($[\text{1}] = 0.003$ mol/l, $\text{Al/Fe} = 50$). All signals of the initial tridentate ligand are retained in the ^1H NMR spectrum of complex **2**, but their position changes substantially (Table 1, spectrum 2). In addition, a new signal (X) with a chemical shift of 38.8 ppm appears in the spectrum. Its intensity corresponds to the presence of two additional (as compared to complex **1**) methyl groups in complex **2**. As shown below, signal X belongs to the AlMe_2 fragment. Complex **2** is stable, and its concentration changes insignificantly over 5 h at room temperature.

When toluene- d_8 is used as a solvent instead of CD_2Cl_2 , complex **2** dominates the **1**/MAO-2 system only at relatively low Al/Fe ratios (lower than 50). At higher ratios (higher than 500), new complex **3** dominates the solution (Fig. 2). The signals from complexes **2** and **3** are designated in Fig. 2 by letters with the corresponding figures in parentheses. Note that, when the CD_2Cl_2 solvent is replaced by toluene, the position of the signals from complex **2** changes insignificantly. The ^1H NMR spectrum of complex **3** exhibits signals of the initial ligand (Table 1, spectrum 5). The signal of protons of Ar-Me in complex **3** (12 H) is masked by an intense signal from MAO. As in the case of complex **2**, the spectrum of complex **3** has an additional signal at 30.9 ppm (6 H) from the AlMe_2 fragment designated in Fig. 2 as X (**3**).

Interaction of 1 with AlMe₃ and Al(CD₃)₃

When **1** reacts with AlMe_3 in CD_2Cl_2 ($\text{Al/Fe} = 100$) at a low temperature (−80 to 0°C), the starting complex is almost completely transformed into new complex **4**. Complex **4** is less stable in the **1**/ AlMe_3 system in CD_2Cl_2 than complexes **2** and **3** in the **1**/MAO system in toluene, and its signals in the spectrum disappear at 0°C. The chemical shifts of all five signals of complex **4** in CD_2Cl_2 are unexpectedly close to the corresponding signal from complex **3** in toluene- d_8 (Table 1). Thus,

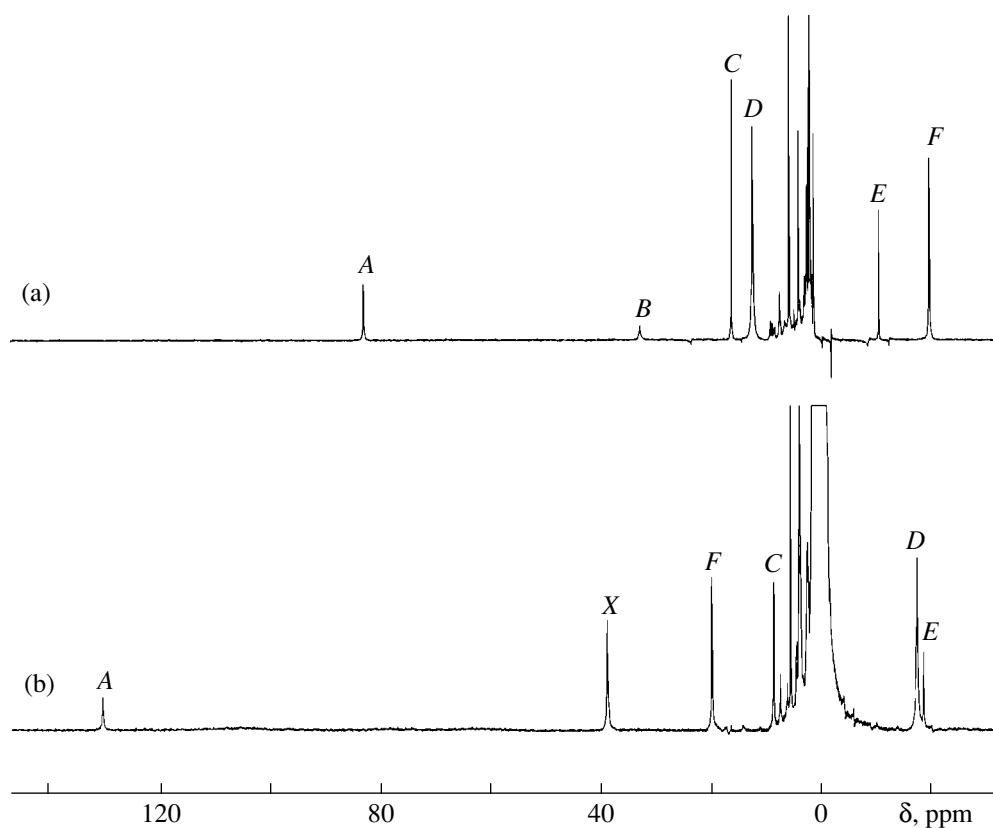


Fig. 1. ^1H NMR spectra of (a) starting complex **1** and (b) complex **2** generated in the reaction of **1** with MAO-2 in CD_2Cl_2 at 20°C ($[\mathbf{1}] = 0.003 \text{ mol/l}$, $\text{Al/Fe} = 50$).

complexes **3** and **4** are either identical or very close in their structures. Since complex **4** is formed in the $\mathbf{1}/\text{AlMe}_3$ system in which the formation of cation-like structures is impossible, we assume that **3** and **4** are

neutral complexes. To establish their structure, we studied the ^2H NMR spectrum of complex **4**, which is generated in the reaction of **1** with $\text{Al}(\text{CD}_3)_3$ at -30°C (Fig. 3). This spectrum contains two signals with equal

Table 1. Chemical shifts (ppm) in ^1H NMR spectra of complexes **1–6***

Spectrum no.	Complex	Solvent	$T, ^\circ\text{C}$	A (Py- H_m)	B (Py- H_p)	C (Ar- H_m)	D (Ar-Me)	E (Ar- H_p)	F N=C(Me)	X (Al-Me)
1	1	CD_2Cl_2	20	82.9	32.6	15.9	12.1	-10.8	-20.0	n/a
2	2	CD_2Cl_2	20	130.3	6.1	8.5	-17.6	-18.8	19.7	38.8
3	2	Toluene- d_8	20	126.6	—	8.1	-14.7	-19.8	21.6	38.3
4	2	Toluene- d_8	-10	153.9	—	—	-25.0	-25.2	21.6	51.4
5	3	Toluene- d_8	20	107.2	-36.1	16.0	—	-10.9	20.0	30.9
6	3	Toluene- d_8	-10	127.0	-44.9	18.2	—	-13.6	19.4	37.3
7	4	CD_2Cl_2	-10	125.0	-42.8	18.3	—	-13.3	18.4	35.5
8	5	CD_2Cl_2	10	148.4	—	7.7	-35.9	-21.2	—	42.7
9	5	CD_2Cl_2	-10	165.9	—	—	-45.0	-24.1	—	45.7
10	6	CD_2Cl_2	10	141.8	—	7.6	-23.2	-21.3	19.5	44.2
11	6	CD_2Cl_2	-10	157.3	—	6.8	-29.5	-24.1	19.2	51.5

Note: Designations: Py- H_m , two hydrogen atoms in the *meta* positions of pyridyl; Py- H_p , the hydrogen atom in the *para*-position of pyridyl; Ar- H_m , four hydrogen atoms in the *meta* positions of the aromatic cycle; Ar-Me, 12 hydrogen atoms of methyl groups at the aromatic cycle; Ar- H_p , two hydrogen atoms in the *para* positions of the aromatic cycle; N=C(Me), six hydrogen atoms of methyl groups at the N=C bond; and Al-Me, AlMe_2 fragment.

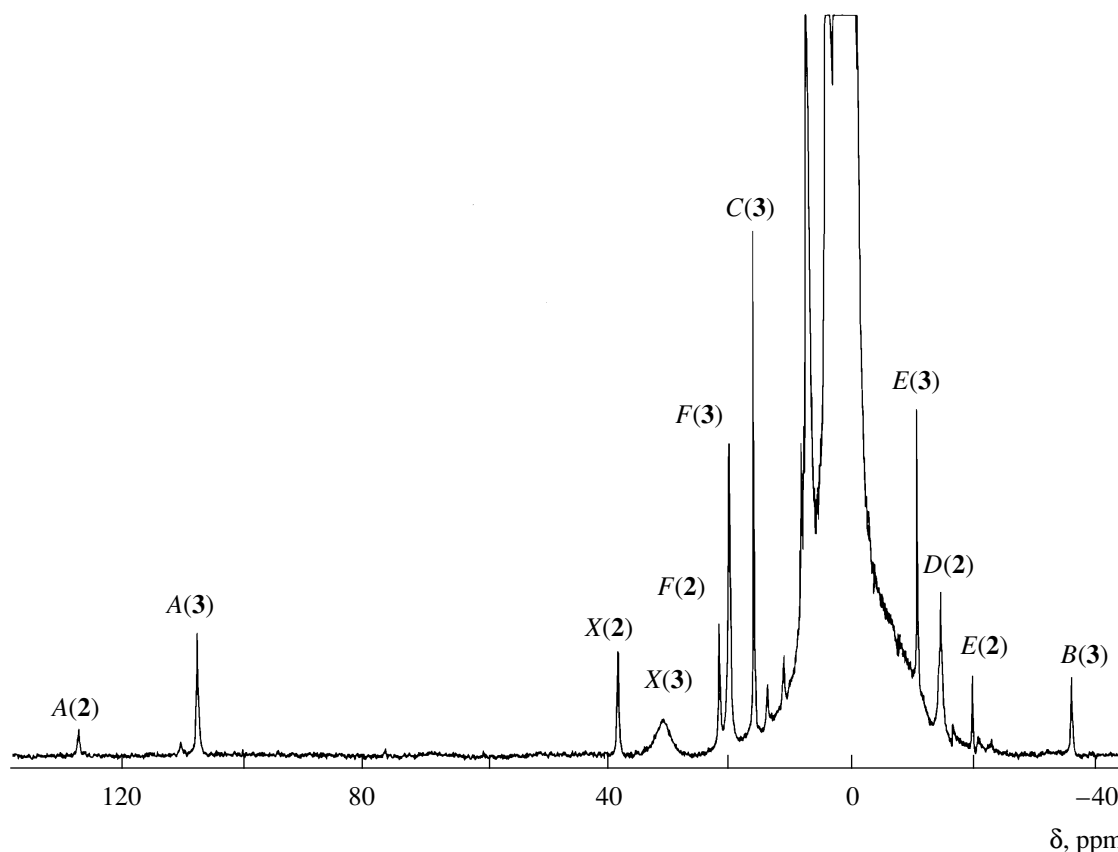


Fig. 2. ^1H NMR spectrum of complexes **2** and **3** generated in the reaction of **1** with MAO-2 in toluene- d_8 at 20°C ($[\mathbf{1}] = 0.0003 \text{ mol/l}$, $\text{Al/Fe} = 500$).

integral intensities: one signal (47 ppm) from the $\text{Al}(\text{CD}_3)_2$ fragment and another (610 ppm) from two $\text{Fe}(\text{II})\text{--CD}_3$ fragments. The ^2H NMR signal from the CD_2 group of the $(\text{TMEDA})\text{Fe}^{\text{II}}(\text{CD}_2\text{--Ph})_2$ complex, where TMEDA is $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2$, has previously been observed at 1000 ppm [5] in agreement with our data. We failed to observe the ^1H NMR signal from the $\text{Fe}(\text{II})\text{--Me}$ fragment due to a larger paramagnetic broadening of the line than that in the ^2H NMR spectrum. The spectroscopic data suggest that **3** and **4** represent the neutral complex $\text{LFe}(\text{II})(\text{Me})(\mu\text{--Me})_2\text{AlMe}_2$, and **2** is the $\text{LFe}(\text{II})(\text{Cl})(\mu\text{--Me})_2\text{AlMe}_2$ complex, where L is the starting bis(imine)pyridine ligand (Fig. 4). We failed to detect the signal of the terminal methyl group of complexes **3** and **4** in the ^1H and ^2H NMR spectra.

*Interaction of **1** with $\text{AlMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{AlMe}_3/\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$*

Immediately after the mixing of reactants in the $\mathbf{1}/\text{AlMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ system at -20°C , complex **1** transforms into new complex **5**, and in the $\mathbf{1}/\text{AlMe}_3/\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$ system new complex **6** is formed (Fig. 5) (the ratio of reactants is 1 : 100 : 1). The chemical shifts of the corresponding signals of complexes **5** and **6** are close to each other and differ consid-

erably from those of the same signals in complex **4** at the same temperature (Table 1). As shown above, the reaction of **1** with AlMe_3 creates complex **4**. Therefore, complexes **5** and **6** are generated in the reaction of **4** with $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$, respectively. A typical reaction of the activators under consideration with the methylated metal complex is the elimination of the methyl anion to form ion pairs [6–8]. That is why complexes **5** and **6** are probably the ion pairs $[\text{LFe}(\text{II})(\mu\text{--Me})_2\text{AlMe}_2]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{LFe}(\text{II})(\mu\text{--Me})_2\text{AlMe}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, respectively.

Ethylene Polymerization in the Presence of the $\mathbf{1}/\text{MAO}$, $\mathbf{1}/\text{AlMe}_3$, and $\mathbf{1}/\text{AlMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ Catalytic Systems

The data on ethylene polymerization are presented in Table 2. The activity of the $\mathbf{1}/\text{MAO}$ catalyst decreases dramatically (almost 20-fold) with a decrease in the residual trimethylaluminum concentration in MAO (Table 2, rows 1 and 2). At equal Al/Fe molar ratios, the activity of the $\mathbf{1}/\text{AlMe}_3$ system was much higher than that of the $\mathbf{1}/\text{MAO-1}$ system and, especially, $\mathbf{1}/\text{MAO-3}$ (Table 2, rows 1–3). A decrease in the concentration of AlMe_3 in the polymerization medium leads to a decrease in the catalytic activity of the system (rows 3–5).

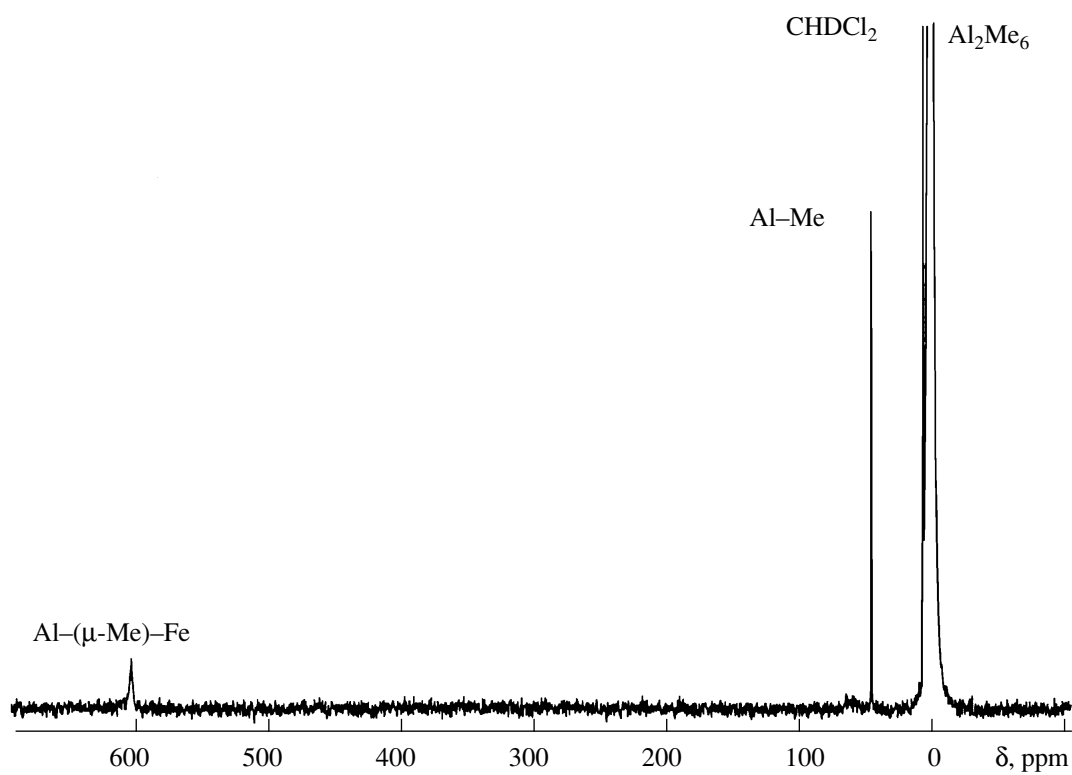


Fig. 3. ^2H NMR spectrum of complex **4** generated in the reaction of **1** with $\text{Al}(\text{CD}_3)_3$ in CD_2Cl_2 at -50°C ($[\textbf{1}] = 0.001 \text{ mol/l}$, $\text{Al/Fe} = 100$).

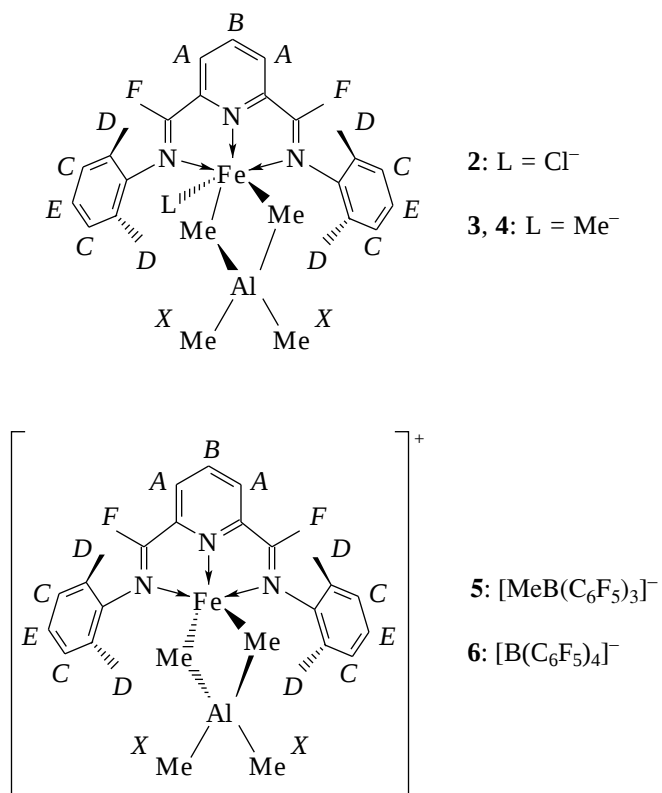


Fig. 4. Assumed structures of complexes **2**–**6**.

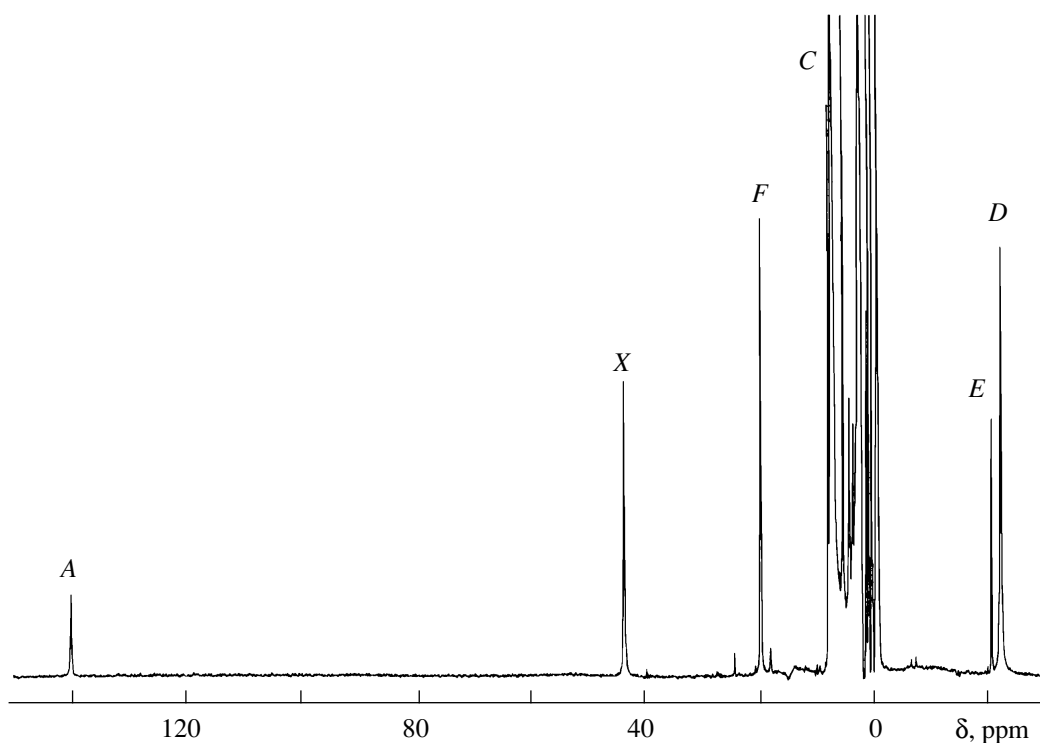


Fig. 5. ^1H NMR spectrum of complex **1** in CD_2Cl_2 at 10°C after its reaction with $\text{AlMe}_3/\text{CPh}_3\text{B}(\text{C}_6\text{F}_5)_4$ ($[\mathbf{1}] = 0.003 \text{ mol/l}$, $\text{Al/Fe} = 100$).

When $\text{B}(\text{C}_6\text{F}_5)_3$ is added to the $\mathbf{1}/\text{AlMe}_3$ system, the catalyst activity somewhat increases (rows 5 and 6). The kinetic curves of ethylene polymerization in the presence of $\mathbf{1}/\text{MAO}$, $\mathbf{1}/\text{AlMe}_3$, and $\mathbf{1}/\text{AlMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ are very close. All these systems are characterized by the high initial activity, which drops 15 min after the beginning of polymerization. The polymer samples have an analogous linear structures and close numbers of methyl groups ($\sim 3 \text{ CH}_3$ groups per 1000 carbon atoms) and terminal vinyl groups (~ 0.8 per 1000 carbon atoms).

The participation of the $\mathbf{1}/\text{AlMe}_3$ and $\mathbf{1}/\text{AlMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ catalysts with the ratio $\text{Al/Fe} = 100$ gives polymers with close molecular weights (see melt indices in Table 2, rows 5 and 6). It is well known that AlMe_3 is an efficient chain carrier, and an increase in its concentration leads to a decrease in the molecular weight of the polymer. This can be the reason for an increase in the melt index of the polymer with an increase in the Al/Fe molar ratio from 100 to 500 (Table 2, rows 3 and 5).

Table 2. Ethylene polymerization in the presence of complex **1** with various cocatalysts (solvent toluene, 35°C , ethylene pressure 5 atm, time 60 min, $[\text{Fe}] = 1.3 \times 10^{-5} \text{ mol/l}$)

No.	Cocatalyst	Al/Fe	Yield of polyethylene, g	Activity, (kg PE) (mol Fe) $^{-1} \text{ h}^{-1} \text{ atm}^{-1}$	MI*, g/10 min
1	MAO-1	500	37.2	3720	13.4
2	MAO-3	500	2.0	200	–
3	AlMe_3	500	59.0	5900	>100
4	AlMe_3	250	11.4	1140	32
5	AlMe_3	100	5.1	510	26
6	$\text{AlMe}_3 + \text{B}(\text{C}_6\text{F}_5)_3$	100	7.2	720	23
		1			

* Melt indices of polyethylene samples measured at 190°C and a load of 2.16 kg.

Possible Structures of Active Polymerization Centers

The catalytic data (Table 2) indicate that the **1**/AlMe₃ and **1**/MAO catalytic systems contain probably the same active component, which is generated in the reaction of **1** with AlMe₃. Complex **4** (Fig. 4) is most likely the closest precursor of these active species. To transform complex **4** into a species that carries polymerization, the coordination site for an ethylene molecule must be freed. The mechanism for this transformation is still unclear. The active components are neutral rather than cation-like structures because the formation of these structures in the **1**/AlMe₃ system is improbable. The authors of [9] have recently shown that the neutral Ni(II) complex with a Schiff base containing a methyl ligand is capable of carrying ethylene polymerization without cocatalyst additives and is not worse than the best known catalytic systems in its activity.

According to NMR data, the structures of complexes **5** and **6** differ from that of complex **4**. However, the data in Table 2 do not suggest that the **1**/AlMe₃/B(C₆F₅)₃ catalytic system contains any active centers different from those in the **1**/AlMe₃ system.

CONCLUSION

Thus, the use of ¹H and ²H NMR spectroscopy revealed the structure of the Fe(II) complexes generated in the activation of the Fe(II)-based catalysts of ethylene polymerization with various cocatalysts (MAO, AlMe₃, AlMe₃/B(C₆F₅)₃, and AlMe₃/CPh₃B(C₆F₅)₄). The cata-

lytic and NMR data indicate that the neutral rather than cationic complexes are the key intermediates of the **1**/MAO and **1**/AlMe₃ catalytic systems.

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